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Study of heteroatom effect on graphitic carbons derived from anthracene phenanthrene-sulphur system by thermal and optical analysis

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Abstract The carbonaceous mesophase as a precursor to graphitization has been examined from polynuclear organic compounds, such as anthracene-sulphur and phenanthrene-sulphur systems with the aid of Differential Thermal Analysis (DTA), Thermogravimetric Analysis (TGA) and finally by the polarized-light technique. With the continued addition of sulphur-hydrogen mole ratio, the latent heat of fusion (i.e. activation energy) and as such the graphitizability of the carbons have been found to decrease. In addition to dehydrogenation, sulphur caused crosslinking between layer planes thus preventing the formation of oriented layers, typical of the graphite structure.

Keywords Heteroatom, Mesophase, DTA, TGA, Latent heat of fusion, Polarized light

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1. Introduction

Though the study of carbon is an old subject but now it comes with a new approach to the graphite manufacturers. Synthetic manufacture of graphite from organic compounds, higher rank coal, coal tar pitches etc. can be guessed in the early stages of carbonization from 350^{0}C to 600^{0}C. This is the liquid or plastic state transition or mesophase during which large planar aromatic molecules become aligned in a parallel array to form an optically anisotropic liquid crystal [1-8]. In the initial stages of nucleation and growth, the mesophase appears as spherules and as carbonization progresses with increasing temperature and heat-treatment duration, the growing mesophase spherules coalesce and change in shape in forming plastic flow patterns. The nucleation, growth and coalescence processes of the mesophase spherules establish the basic elements of the graphite microstructure [9-11].

The potential role of heteroatoms, such as N_2, O_2 and S in controlling the carbonization and graphitization of coals, organic molecules and polymers has been appreciated for many years. Non-carbon elements such as O_2, N_2 and S have a deleterious influence on the growth and coalescence of mesophase microstructure. These heteroatoms can form in part stable volatile by products, thus reducing the carbon yield. On the other hand, the heteroatoms can affect cross-linkage in the compound. In this fashion they will reduce the vapour pressure and cause coking in the liquid and especially in the solid phase. This effect will increase the carbon yields [12]. This paper describes the study of heteroatom effect on carbonization and ultimately the graphitization of polynuclear organic compounds.

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2. Experimental

2.1 Preparation of samples

Pure anthracene and phenanthrene (AR grade 99%, E-merck) samples were intimately mixed with sulphur in mole ratios of S/H = 1/10, S/H = 2/10, S/H = 3/10, S/H = 4/10 for anthracene and S/H = 1/16, S/H = 1/8, S/H = 1/4 and S/H = 3/8 for phenanthrene respectively. Carbonization was carried out by the sealed-tube technique [13] and the resulting carbons were then embedded in cold-setting mounting resins for polishing. Polishing technique has been described elsewhere [14-15].

2.2 Differential thermal analysis (DTA) and Thermogravimetric analysis (TGA) :

Details of the technique have been described elsewhere [16]. A Shimadzu micro DTA, TGA system model DT-30 manufactured by Shimadzu Corporation Kyoto, Japan were used in the present investigation. All experiments were run at atmospheric pressure and in a continuous flow of nitrogen gas. The TGA was used for quantitative analysis of the sample.

2.3 Polarized-light technique :

The sample prepared as in art 2.1 are observed and photographed with a Reichert Metavert polarizing microscope equipped with the 35mm Remica III photographic camera.

2.4 Latent heat of fusion :

The latent heat of fusion is calculated from the 1st endothermic peak area of the DTA curves [17]. The peak area can be obtained with a planimeter or by weighing the cut out area of the curve drawn on transparent paper [18]. In this case, the peak area is cut out and weighed in an electronic balance. This weight is then compared with that of peak area obtained for a standard reference sample benzoic acid.

3. Results and discussion

The results of the DTA and TGA both for anthracene-sulphur and phenanthrene-sulphur system can be interpreted as follows In the DTA traces (Figures 1 and 2), the initial endotherms become narrower with the addition of sulphur indicating that it is acting here as a catalyst for cross-linking. The latent heat of fusion for the respective mixtures gradually decreases with the addition of sulphur which means the consequent decrease of activation energy [19] and hence the graphitizing power. Figures 3 and 4 show the effect of latent heat of fusion.

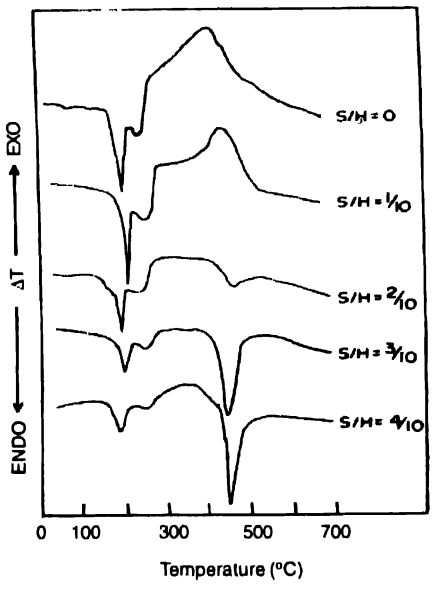

Figure 1. DTA traces of anthracene-sulphur mixtures in different S/H ratios

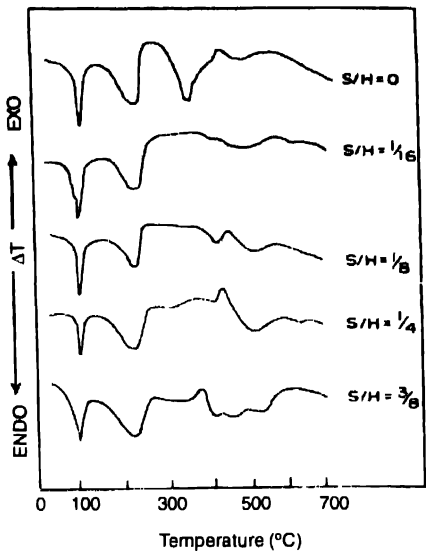

Figure 2. DTA traces of phenanthrene-sulphur mixtures in different S/H ratios

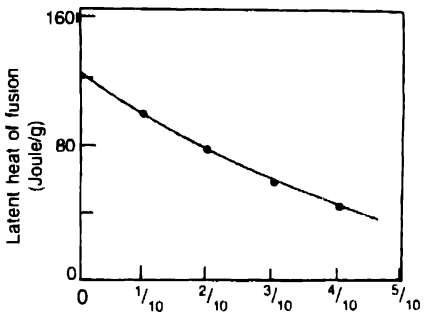

Figure 3. The latent heat of fusion decreases with the different S/H ratios of anthracene-sulphur mixtures

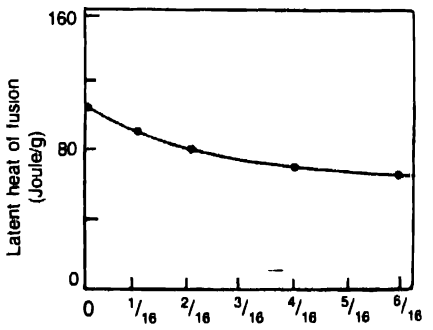

Figure 4. The latent heat of fusion decreases with the different S/H ratios of phenanthrene-sulphur mixtures.

At a sufficiently high temperature the addition product may be expected to aromatize by elimination of hydrogen, hydrocarbons and other gases, such as H_2S, CS_2, CH_4, C_2H_6 *etc.* by the process of Diels-Alder type reaction. The Diels-Alder reaction itself may be expected to facilitate.

A probable mechanism of catalytic action developing cross-linking is presented in such a way that the basic function of sulphur is to generate unsaturated centers, which can initiate chain dehydrogenation. the formation of large condensed system rather than random isolated ring [20]. Figure 5 shows the cross-linking mechanism.

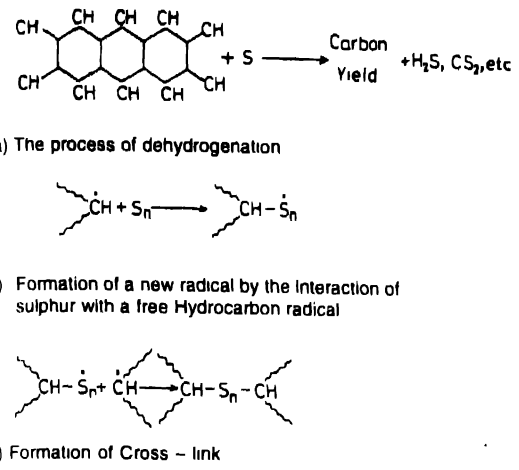

Figure 5. Cross-linking mechanism

The incorporation of some of the sulphur into the structure probably arises because of the interaction of sulphur with free radical centres. During the process of dehydrogenation, high concentration of free radicals will occur, which can react with another hydrocarbon radial to form a cross-link

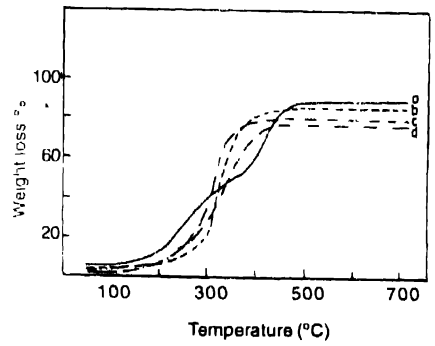

Figure 6 TGA traces of anthracene-sulphur mixtures in different S/H ratios (a) S/H=0 (b) S/H = 1/10 (c) S/H = 2/10 (d) S/H = 3/10

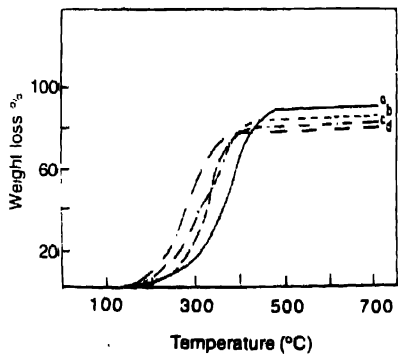

Figure 7. TGA traces of phenanthrene-sulphur mixtures in Different S/H ratios (a) S/H = 0 (b) S/H 1/16 (c) S/H = 1/8 (d) S/H = 1/4.

The weight losses of the samples started from the melting temperature of the samples and continued upto the coalescene temperature by the elimination of hydrogen and hydrocarbon gases, such as H_2S, CO_2 and also by oxidation, decomposition, destruction of crystalline lattice *etc*. From a thermodynamic standpoint, an increase in temperature tends to melt a solid and produce a less ordered system, while an increase in pressure tends to maintain an ordered phase. This creates the possibility that an isotropic liquid phase of a carbonizing system may be favourably transformed, under pressure, into an optically anisotropic liquid crystal. In the TGA results, the carbon yield is increased with the addition of sulphur, which is supported by Blayden's assumption [12].

The carbons obtained by pyrolysis are relatively soft, black, shining and are of low microporosity possess graphitic carbon, while relatively hard, low apparent density, high microporosity possess the non-graphitizing carbons [2-3]. Figures 8 and 9 show physical appearance of graphitizing and non-graphitizing carbon produced from anthracene.

Figure 8. Physically appearing graphitizing carbon produced from anthracene at 430°C for 4 hours carbonization.

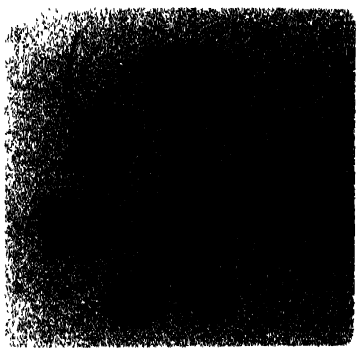

Figure 9. Physically appearing non-graphitizing carbon produced from anthracene-sulphur mixture (S/H=3/10) 490°C for 4 hours carbonization.

The graphitizing nature of carbons have been found upto the critical ratio S/H = 2/10 for anthracene and S/H = 1/4 for

phenanthrene. Figure 10 shows the mesophase spherules of anthracene-sulphur mixture S/H = 0 at 460^{0}C for 4 hours.

Figure 10. Mesophase spherules of anthracene-sulphur mixture (S/H=0) at 460°C for 4 hours

Figure 11. Ruptured mesophase spherules of anthracene-sulphur mixture (S/H=3/10) at 490°C for 4 hours

Figure 12. Mesophase spherules of phenanthrene-sulphur mixture (S/H=0) at 530°C for 5 hours

Ruptured mesophase spherules from anthracene-sulphur mixtures is shown in Figures 11 for S/H = 3/10 at 490^{0}C for 4 hours heat-treatment duration. For phenanthrene, Figure 12 and 13 show the mesophase spherules and most distorted spherules for the ratios of S/H = 0 and S/H = 3/8 at 530^{0}C and 560^{0}C for 5 hours heat treatment duration.

Figure 13. Distorted spherules developed in Phenanthrene-sulphur ratio S/H=3/8 at 560°C for 5 hours

4. Conclusions

The heteroatom plays a significant role in controlling the growth of graphitic carbon, an anisotropic three-dimensional ordering structure. As the amount of sulphur added is increased the temperature range of fusion becomes shorter due to the formation of higher degree of cross-linking, which also prohibit the degree of graphitization. Most ruptured and distorted anisotropic structures are found above the critical value of S/H = 2/10 for anthracene and of S/H = 1/4 for phenanthrene. So the polarized light micrography shows the gradual decrease in the extent of orientation with increasing amounts of sulphur.

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